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14. ABSTRACT
This AFOSR grant concentrated on the fabrication of nanolaminates with ultrathin nanolayers using atomic layer deposition (ALD) and molecular layer deposition (MLD) techniques. Nanolaminates are multilayered thin film structures with nanometer dimensions and very high interfacial density. These multilayer structures can display novel properties that can be optimized by manipulating the thickness and composition of the individual nanolayers. During this grant, the research examined nucleation and growth issues involved in the fabrication of W/Al2O3 nanolaminates. These studies are important because W/Al2O3 nanolaminates are important for thermal barrier coatings and x-ray mirrors. Subsequent studies examined SiO2/Al2O3 nanolaminates for gas diffusion barriers on polymers. The brittleness of these SiO2/Al2O3 nanolaminates motivated new work on molecular layer deposition (MLD) to develop flexible nanolaminate films using polymeric interlayers. New MLD growth methods were used to fabricate organic-inorganic nanolaminates that may serve as excellent flexible coatings. The characterization of these organic-inorganic nanolaminates then revealed that cracking of the inorganic nanolayers could be a problem. Flexibility without cracking is essential

15. SUBJECT TERMS
Atomic layer deposition, thin films, multilayer and nanolaminate films, molecular layer deposition, flexible films, gas diffusion barriers, critical strain for cracking, mechanical properties of thin films

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Final Technical Report

February 2009

Fabrication of Nanolaminates with Ultrathin Nanolayers Using Atomic Layer Deposition: Nucleation & Growth Issues

AFOSR Grant No. FA9550-06-1-0075

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I. Overview/Objectives

Our AFOSR grant focused on the fabrication of nanolaminates with ultrathin nanolayers using atomic layer deposition (ALD). Nanolaminates are multilayered thin film structures with nanometer dimensions and very high interfacial density. These multilayer structures can display novel properties. These special properties can be optimized by manipulating the thickness and composition of the individual nanolayers.

We initially focused on the various nucleation and growth issues involved in the fabrication of W/Al_2O_3 nanolaminates. The W/Al_2O_3 nanolaminates are important for thermal barrier coatings and x-ray mirrors. We then turned our attention to SiO_2/Al_2O_3 nanolaminates for gas diffusion barriers on polymers. The brittleness of these SiO_2/Al_2O_3 nanolaminates motivated new work on molecular layer deposition (MLD) to develop flexible nanolaminate films using polymeric interlayers.

Our AFOSR-sponsored research has shown that the optimized nanolaminates have important applications as protective thermal barrier coatings, high reflectivity x-ray mirrors and high performance gas diffusion barriers. As we concluded the current AFOSR grant, we began to explore organic-inorganic nanolaminates that may serve as excellent flexible coatings. Flexibility without cracking is essential for films on flexible polymers.

The understanding of film cracking on flexible polymers is very limited. Consequently, we have explored the relationships between film cracking and tensile and compressive strain. We have also explored the mechanical properties of MLD films using nanoindenter studies. These mechanical properties are important to understand the critical strain for cracking of nanolaminates. These studies will hopefully lead us to the fabrication and optimization of flexible coatings for barrier and protective coating applications..

II. Research Topics

Over the three years, our AFOSR effort has eoncentrated on the following topics:

- Fabrieation of W/Al_2O_3 nanolaminates for high-refleetivity x-ray mirrors on both flat and flexible substrates. We produeed extremely high refeetivity x-ray mirrors.
- Optimization of methods to deposit laterally-graded ALD films for x-ray optical applications. The "moving slit" reaetor design was thoroughly evaluated and its dependenee on various reaction parameters was explored to determine the best way to deposit a laterally-graded ALD film.
- Understanding the nueleation of W ALD on Al_2O_3 substrates. We discovered phenomena that were consistent with initial W ALD island growth during nucleation.
- Development of Al_2O_3/SiN bilayers and multilayers as gas diffusion barriers on polymers. The addition of SiO_2 to the Al_2O_3 layer was needed to prevent H_2O corrosion. The multilayer barriers also produced much lower gas permeability.
- Development of $Al_2O_3/MLD/Al_2O_3$ trilayers as gas diffusion barriers on polymers. Compared with single Al_2O_3 ALD barriers, the H_2O gas permeability was improved using the $Al_2O_3/MLD/Al_2O_3$ trilayers. However, the $Al_2O_3/MLD/Al_2O_3$ trilayers did not show improved mechanical properties.
- Understanding of film cracking for inorganic films on polymer substrates under tensile strain. Measurement of critical strain for cracking using 4-point probe resistivity measurements for eondueting ZnO ALD films and H_2O permeability measurements for insulating Al_2O_3 ALD films.
- Understanding of film eraeking for inorganie films on polymer substrates under compressive stress. Measurement of critieal stress for cracking using field-emission scanning elcetron microscopy (FE-SEM).
- Construction of new experimental apparatus based on ALD reaetor, glovebox and physical vapor deposition (PVD) chamber all connected together. This new apparatus allows Ca test eells to be formed in the PVD chamber and then used to test gas diffusion barriers fabricated in ALD reaetor.

- Understanding of the difference between the HTO test and Ca test for measuring the water vapor transmission rate (WVTR) through ALD-coated polymers.
- Development of new surface chemistry for polymer growth using ALD methods. This work focused on new "alucone" films deposited using $Al(CH_3)$ and various organic diols. These unique organic-inorganic polymers may be useful as flexible interlayers between inorganic layers to fabricate a flexible barrier.
- Continued collaborations with a variety of groups using ALD and MLD for modification or enhanced performance of various substrates and micro- and nano-structures.

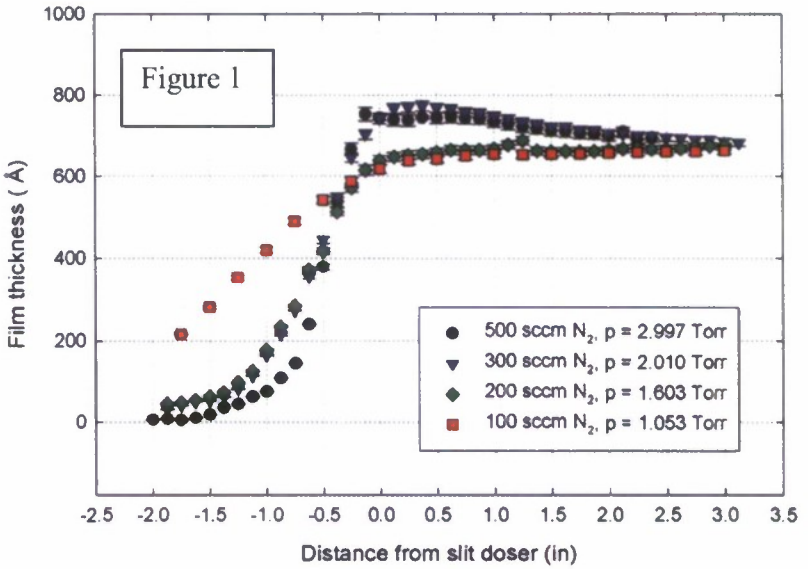
We have made excellent progress over the last three years on these research topics. The majority of our research effort was conducted by Dr. Arrelaine Dameron and Dr. Shih-Hui Jen, postdoctoral research associates, and Dragos Seghete and Jacob Bertrand, two graduate students. Arrelaine worked on the Al_2O_3/SiO_2 nanolaminate gas diffusion barriers and the new alucone MLD surface chemistry. After Arrelaine left the research group, Shih-Hui continued the barrier research and also made the FE-SEM measurements of film cracking resulting from compressive stress. Dragos Seghete initially worked on laterally graded ALD layers and subsequently has worked to use ALD and MLD to make novel nanostructures for nano electromechanical systems (NEMS). Jake Bertrand has built the new Ca test apparatus and studied film cracking under tensile strain using 4-point probe conductivity measurements. Jennifer O'Patchen, an undergraduate researcher, has worked with Jake Bertand on film cracking under tensile strain.

III. Accomplishments/ New Findings

A. Laterally Graded ALD Multilayers

Laterally-graded optics are required for many applications in x-ray optics including x-ray lasers and x-ray microscopes. Laterally-graded multilayers have a bilayer spacing that continuously changes versus spatial position. To obtain laterally graded multilayers using atomic layer deposition (ALD) techniques, the normal conformality of ALD must be circumvented by preventing ALD on the entire substrate. Laterally graded multilayers can be fabricated using a "slit doser" to localize reactant delivery in a viscous flow gas stream. The substrate is translated relative to the slit doser with a magnetic linear translator. Since the viscous flow entrains the reactants and moves them downstream, substrate translation upstream of the slit doser prevents ALD on the entire substrate.

We initially demonstrated a laterally graded Al_2O_3 ALD film by translating the substrate relative to the slit doser during Al_2O_3 ALD reaction cycles. During the first year of this grant, we completed a detailed study of the dependence of the laterally-graded Al_2O_3 ALD film on reactor parameters. The flow rate of the viscous flow gas stream was a key parameter for obtaining a laterally-graded Al_2O_3 ALD film. Figure 1 shows the step in the Al_2O_3 ALD film thickness versus N_2 flow rates in the reactor for a fixed substrate relative to the slit doser. Negative distances correspond with upstream gas diffusion. In the absence of any upstream gas diffusion, the film thickness should have displayed a unit step at 0.0. Larger N_2 flow rates of 500 sccm were required to obtain a reasonable step edge.



Additional experiments revealed that diffusive upstreaming and a turbulent current at the slit doser were responsible for the upstream Al_2O_3 deposition. Using optimized conditions at a flow rate of 500 sccm, laterally-graded Al_2O_3 ALD films were deposited and evaluated using spectroscopic ellipsometry. These investigations revealed that very precise lateral gradients could be obtained even though the slit doser did not produce ideal unit step edges resulting from diffusive upstreaming and turbulent currents at the slit doser. Figure 2 shows profiles of the lateral gradients formed using Al_2O_3 ALD. Gradients in the range of 50-500 Angstroms per inch could easily be formed by moving the sample relative to the slit doser.

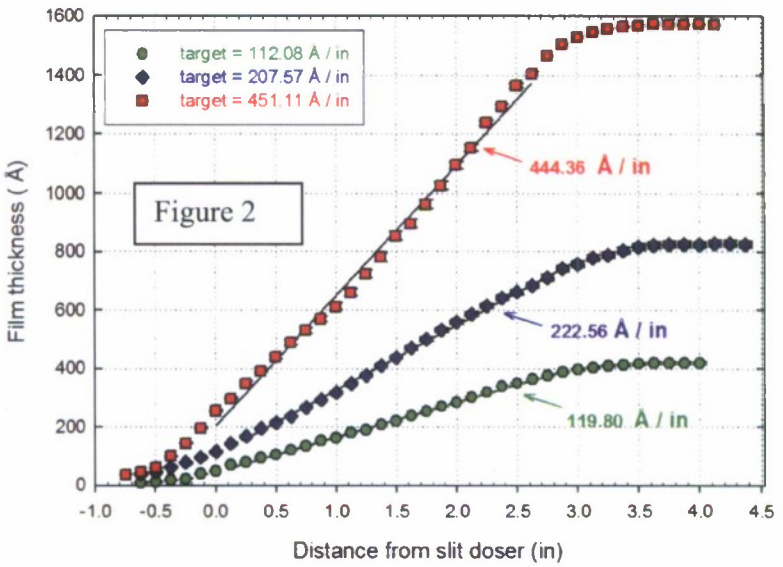
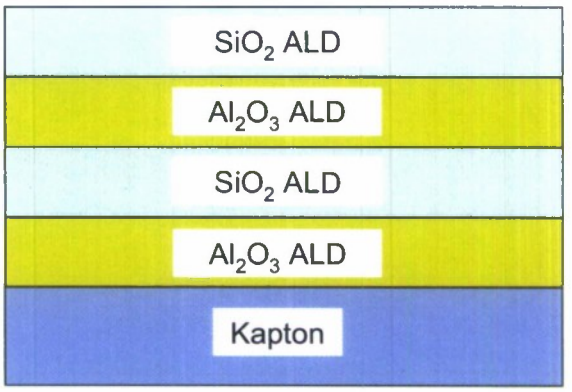


Figure 2

B. Inorganic Nanolaminate Gas Diffusion Barriers on Polymers

During the first year of this grant, we also concentrated n ALD on polymer to fabricate unique gas diffusion barriers on polymers. This work concentrated on thin films on polymers that exhibit exceptionally low H_2O permeability. This low H_2O permeability is critical for the protection of organic light emitting diodes (OLEDs) in flexible polymer displays. Our initial work demonstrated that low water vapor transmission rates (WVTRs) of ~1×10^{-3} g/m^2/day could be achieved on polyethylene naphthalate (PEN) and Kapton® polyimide using a single Al_2O_3 ALD film with a thickness of ~25 nm. However, these H_2O transmission rates are not low enough to meet the

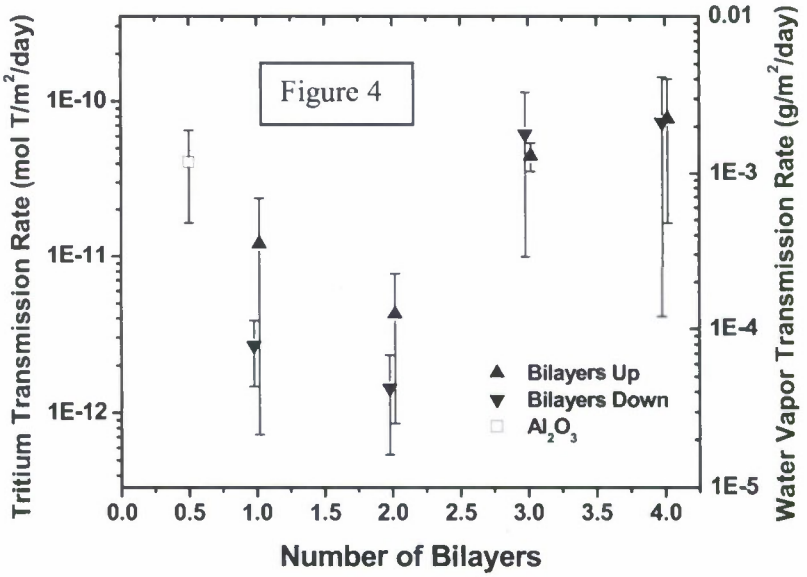
Figure 3



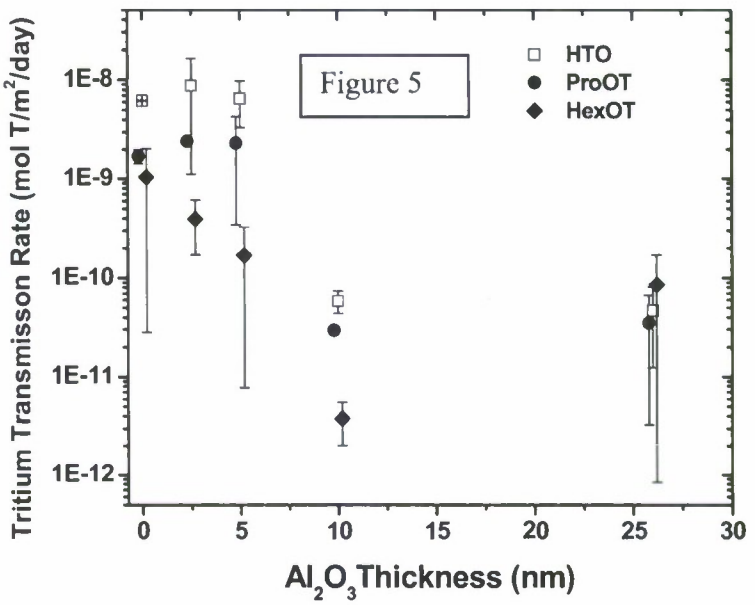
OLED requirement of WVTR ≤ 1 x 10^{-6} g/m^2/day. To lower the H_2O transmission rates further, we have fabricated nanolaminate gas diffusion barriers.

Our work focused on Al_2O_3/SiO_2 bilayers and multilayers of Al_2O_3/SiO_2 bilayers. We first used bilayers defined by the ~25 nm Al_2O_3 ALD layer in combination with a SiO_2 layer with a thickness of ~60 nm deposited using rapid SiO_2 ALD. The SiO_2 layer was important to prevent the H_2O corrosion of the Al_2O_3 ALD layer. The SiO_2 ALD layer eliminated the corrosion problem and the WVTR was reduced by about a factor of 10 to ~1 x 10^{-4} g/m^2/day with this Al_2O_3/SiO_2 bilayer compared with the Al_2O_3 ALD layer by itself. Multilayers of Al_2O_3 ALD/SiO_2 ALD such as the two bilayer Al_2O_3/SiO_2 multilayer shown in Figure 3 were then explored to further reduce the WVTR.

Initial tests of the two bilayer nanolaminates on Kapton® polyimide yielded extremely low WVTRs of ~5 × 10^{-5} g/m^2/day. However, the 3 and 4 bilayer nanolaminates displayed higher WVTRs. The WVTRs versus number of bilayers is shown in Figure 4. Bilayers "Up" refers to bilayers on the polymer facing away from direct HTO vapor exposure during the HTO test. Bilayers "Down" refers to bilayers on the polymer that are in direct contact with the HTO vapor exposures. The increase in the WVTR for the larger number of bilayers may be caused by film cracking because of brittleness at larger film thicknesses. Inorganic films can be very flexible at thicknesses <1000 Å. However, cracking becomes a problem as the film thicknesses increases. To overcome this problem, we started working on nanolaminates of inorganic and flexible organic materials. The flexible organic interlayers should decouple the inorganic layers and prevent the film cracking.



We have also worked with DuPont on testing the ALD-eoated polymers. DuPont measures the WVTR using the Ca test. This optieal test is based on the oxidation of metallie Ca (whieh is refleetive) to $Ca(OH)_2$ and CaO (whieh are transparent). The eomparison between the HTO tests at the University of Colorado and the Ca tests at DuPont have revealed that the Ca test measures lower WVTRs for the same gas diffusion barriers. To understand the differenees between the HTO test and the Ca test, we examined the measured effeetive WVTRs using different tritium sourees.



We found almost the same effeetive WVTRs for HTO and tritiated propanol (ProOT) and tritiated hexanol (HexOT). The tritium transmission rates versus Al_2O_3 ALD film thiekness are shown in Figure 5. The similarity of the tritium transmission rates for the 26 nm Al_2O_3 ALD films argues that the tritium is diffusing through the Al_2O_3 ALD barrier as tritium atoms. We believe that there is rapid H/T exehange between the tritiated moleeules and the surfaee hydroxyl groups on the Al_2O_3 ALD surfaee. The tritium diffusion ean then oeeur through H/T exehange between surfaee hydroxyl groups on the Al_2O_3 surfaee.

In eollaboration with DuPont, we also showed that Al_2O_3 ALD layers on SiN plasma-enhaneed ehemieal vapor deposition (PECVD) layers provided exeellent barrier properties. The H_2O permeabilities measured with the Ca test were at the limit of the glass lid eontrol. This behavior indieated that the ALD/PECVD barriers performed as well as glass. The water vapor transmission rates for Al_2O_3 ALD films of various thieknesses on SiN PECVD films on polyethylene naphthalate (PEN) are shown in Figure 6. The water vapor transmission rate (WVTR) of the initial PEN substrate is ~1 g/m^2/day. For Ca test measurements at 38°C, the WVTR drops almost five orders of magnitude after only 5 nm of Al_2O_3 ALD on the SiN PECVD

film with a thickness of 100 nm on PEN. This WVTR at 38°C after only 5 nm of Al_2O_3 ALD is limited by the Ca test and may be even lower than the Ca test measurement.

We know that the Al_2O_3/SiN barrier has reached the limits of the Ca test because the WVTR of ~1 x 10^{-5} g/m^2/day is the same as the glass lid control measurement. This value is limited by H_2O permeability through the epoxy used to seal the glass lid or Al_2O_3 ALD-coated SiN PECVD film on PEN to the substrate used to perform the Ca test. We believe that even lower WVTR values could be measured if the epoxy seal was also coated with Al_2O_3 ALD to prevent H_2O from entering the test structure.

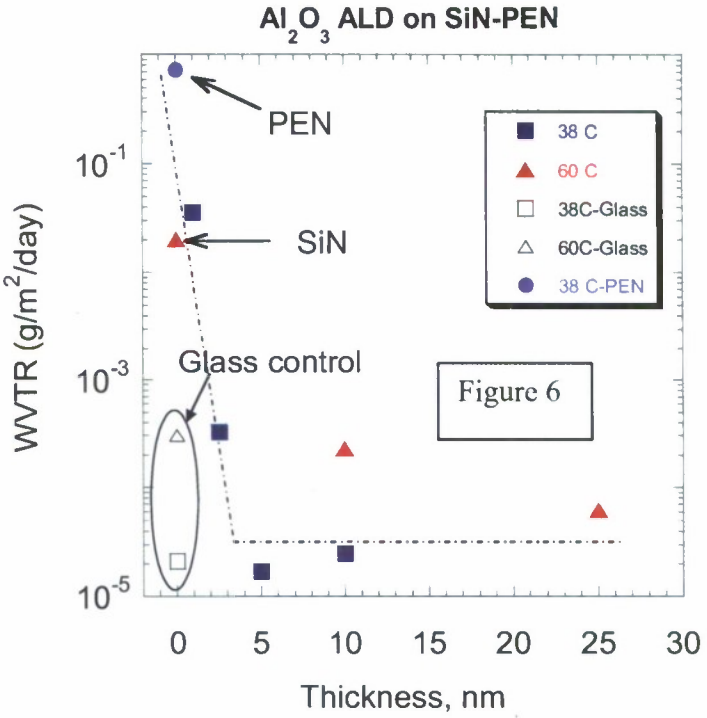
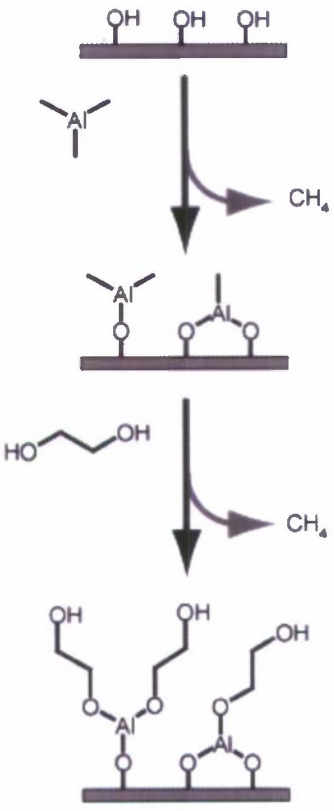


Figure 6

Figure 7



C. Polymeric Interlayers for Flexible Nanolaminates

To develop new flexible, polymeric interlayers for use in building unique flexible nanolaminates, we worked on the development of new sequential, self-limiting surface chemistries for the process known as molecular layer deposition (MLD). MLD is very similar to atomic layer deposition (ALD). The MLD reactants are typically monomers for step-wise condensation polymerization and can yield completely organic or organic-inorganic alloys. We worked to demonstrate the growth

of alucone poly(aluminum ethylene glycol), $[Al\text{-}OCH_2CH_2O]_n$, using the sequential exposures of (A) trimethylaluminum (TMA) and (B) 1,2-ethanediol (ED) as shown in Figure 7.

The AB alucone films have been fabricated at temperatures ranging from 85 °C to 175 °C. Using *in situ* quartz crystal microbalance and *ex situ* x-ray reflectivity experiments, we confirmed the linear growth of the alucone films versus number of TMA/ED reaction cycles at all temperatures. The MLD growth rates decreased at higher temperatures. Growth rates were 4 Å per cycle at 85°C and 1.7 Å per cycle at 135°C. *In situ* and *ex situ* Fourier transform infrared spectroscopy (FTIR) were used to monitor the surface reactions. The AB alucone MLD is very efficient and is compatible with the ALD of many inorganic systems such as Al_2O_3 ALD. We observed that the alucone films are not extremely stable. They shrink versus time and can also absorb additional gases if they are not capped with 3 ALD.

D. Organic-Inorganic Trilayers as Gas Diffusion Barriers

Following the work on inorganic nanolaminates, we begun to explore organic-inorganic nanolaminates as gas diffusion barriers using the newly developed AB alucone MLD. Organic-inorganic nanolaminates are important because they could serve as high performance gas diffusion barriers and also display excellent flexibility. Flexibility without cracking is extremely important for flexible organic electronic devices. We fabricated trilayer films composed of two Al_2O_3 ALD layers with an alucone MLD layer as the interlayer. The AB alucone MLD layer is flexible and displays a modulus of 37 GPa as measured by nanoindenter studies. In contrast, the Al_2O_3 ALD layer is much more brittle and yields a modulus of 165 GPa.

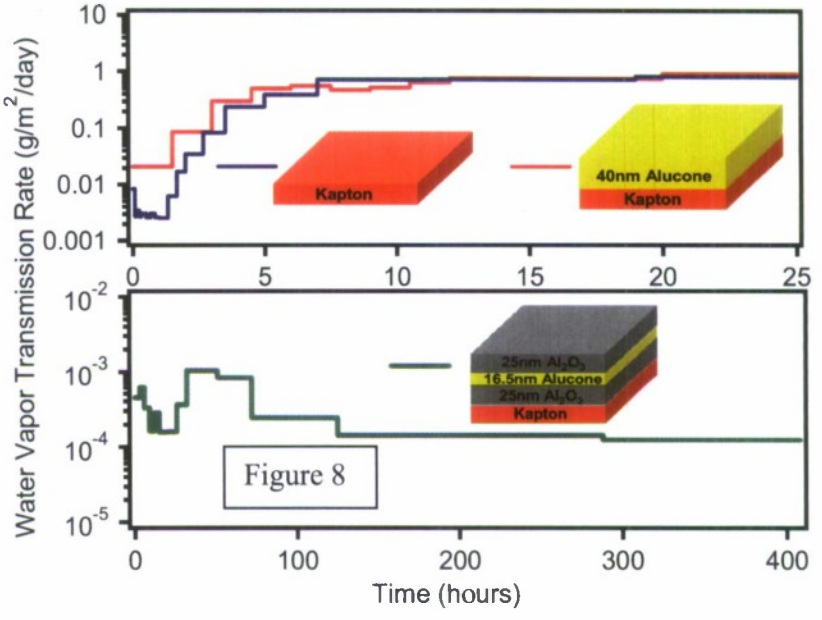


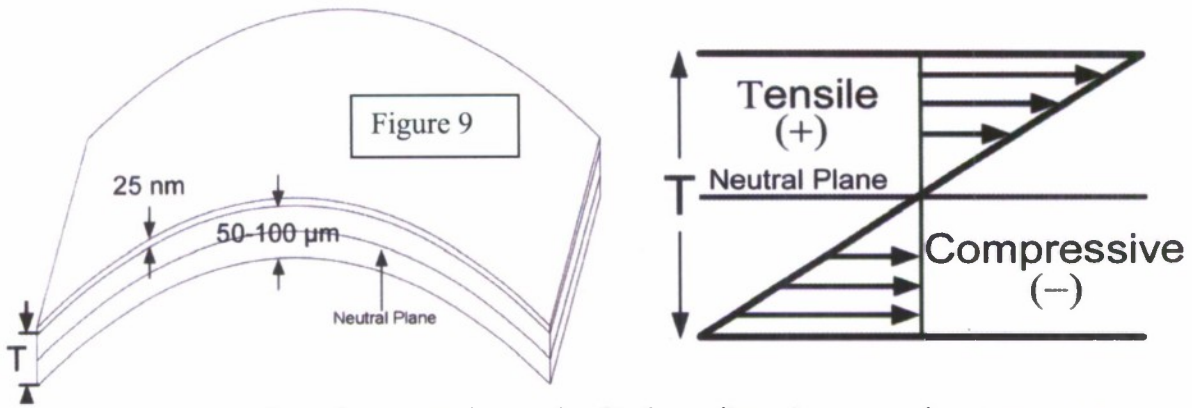
Figure 8

The hope is that the flexible MLD interlayer can decouple the two brittle inorganic layers and allow the trilayer to bend without cracking. HTO test results for the WVTR for Kapton©, AB alucone MLD on Kapton© and the Al_2O_3/ AB alucone MLD/Al_2O_3 trilayer on Kapton are shown in Figure 8. The trilayer reduces the WVTR almost four orders of magnitude. This WVTR is an order of magnitude lower than the WVTR for a 25 nm Al_2O_3 ALD layer on Kapton.

Although the WVTR results for the trilayer are very encouraging, the mechanical properties of the Al_2O_3/AB alucone MLD/Al_2O_3 trilayer were disappointing. The critical tensile strain for cracking of the trilayer was nearly identical to an Al_2O_3 film with the same thickness as the trilayer. These results suggest that the AB alucone MLD layer is not decoupling the two Al_2O_3 ALD layers. We are currently working to use alternative alucone MLD layers in the trilayer structure. One new alucone is the so-called "ABC" alucone that has an even lower modulus of 13 GPa. We hope that this lower modulus will help to decouple the two Al_2O_3 ALD layers to provide a higher critical strain for cracking.

E. Critical Tensile Stress for Film Cracking

The trilayer results introduced us to several important questions for gas diffusion barrier films on polymer substrates: When do inorganic films crack? How does cracking depend on film thickness? Can the critical strain for cracking be increased in multilayer films? To begin to answer the first two questions, we started to measure the cracking of inorganic films on polymer



substrates versus tensile and compressive strain. Both tensile and compressive stresses are experienced during bending. A tensile strain is applied to an inorganic film on top of the bent polymer substrate. In addition, a compressive stress is applied to an inorganic film on the bottom of a bent polymer substrate. Figure 9 shows a bent film and the tensile and compressive

strains on a film on the top or bottom of this bent film. The neutral plane is the plane that does not experience stress during bending.

During the last year of this grant, we measured the critical tensile strain for cracking for Al_2O_3 ALD and ZnO ALD films on polymer substrates. For these studies, we used both optical microscopy to visualize the cracks and electrical resistivity to measure the presence of cracks. Crack densities measured using optical microscopy versus tensile strain for three Al_2O_3 ALD film thicknesses are shown in Figure 10. The results demonstrate that film cracking is very dependent on film thickness. Much *higher* critical strains are observed for *thinner* Al_2O_3 ALD films.

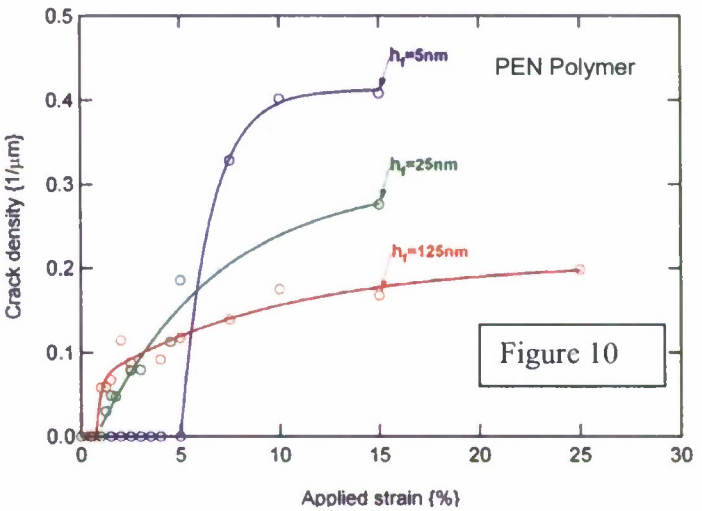


Figure 10

Similar experiments were performed using conducting ZnO ALD films versus tensile strain. The resistivity increases when the film cracks. *Thinner* ZnO ALD films displayed resistivity increases at *higher* critical strains. ZnO ALD films with a thickness of 66 nm displayed a resistivity increase at 1.60% strain. ZnO ALD films with a thickness of 126 nm displayed a resistivity increase at 0.40% strain. Field emission scanning electron microscopy (FESEM) of the ZnO ALD film with a thickness of 66 nm after a 1.75% strain is shown in Figure 11. The cracks are approximately perpendicular to the tensile stress direction. We are still working on these experiments to determine the dependence of critical strain for cracking on film thickness. Although some

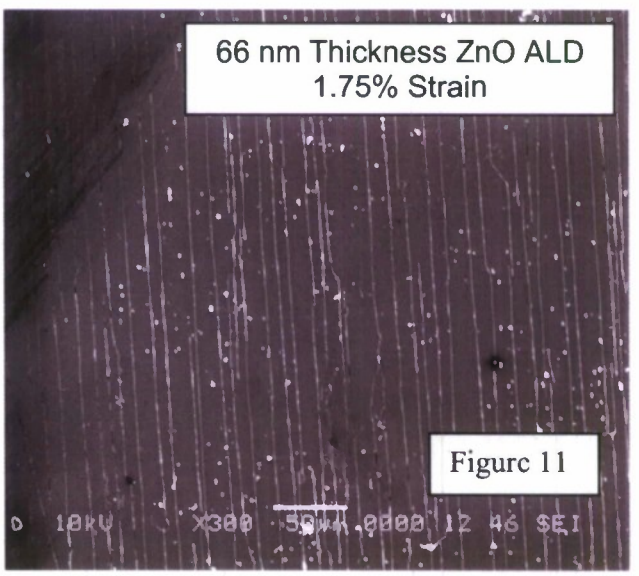


Figure 11

carlier work has explored the critical strain for cracking of indium-tin-oxide (ITO) films used as transparent conducting oxides, very little work has been performed to understand film cracking.

F. Critical Compressive Stress for Film Cracking

Compressive stress is also very important for flexible films. Compressive stress occurs for films on the bottom of a polymer substrate during bending as shown in Figure 9. Compressive stress also occurs when ALD films are cooled to room temperature after deposition at higher temperature. This compressive stress results from the larger thermal expansion of polymers compared with inorganic materials such as Al_2O_3. The polymer contracts more than the ALD film upon cooling to room temperature. This contraction places a compressive stress on the ALD film. Teflon has an especially high thermal expansion coefficient. The difference in thermal expansion coefficient between Teflon and the Al_2O_3 ALD film leads to considerable compressive stress in the Al_2O_3 ALD film upon cooling.

The compressive stress can be calculated from the difference in thermal expansion coefficients for Teflon FEP and Al_2O_3 ALD and the temperature difference, ΔT. The Al_2O_3 ALD film on Teflon FEP can be grown at different deposition temperatures. Consequently, the compressive stress on the Al_2O_3 ALD film upon cooling to room temperature can be easily adjusted by changing the deposition temperature. Various Al_2O_3 ALD film thicknesses have been grown at different deposition temperatures to define the compressive stress.

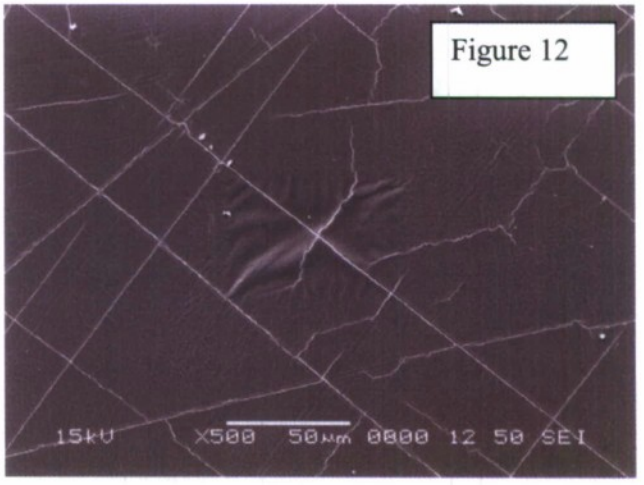


Figure 12

The presence and density of cracks can then be visualized using FESEM analysis. Figure 12 shows an FESEM image (50 µm spatial bar) of an Al_2O_3 ALD film with a thickness of 36 nm grown on Teflon FEP at 160°C. The FESEM shows many interlinking cracks resulting from the compressive stress. An enlargement in Figure 13 (1 µm spatial bar) of the cracks in Figure 12 shows the "folded" crack structure characteristic of compressive stress. The cracks are like

"folds" in a rug after cracking resulting from compressive stress. In contrast, the cracks are "gaps" for tensile strain as shown in Figure 11.

The Al_2O_3 ALD film displays a threshold compressive stress for cracking on Teflon FEP. This threshold compressive stress was determined by growing Al_2O_3 ALD films at different deposition temperatures and then letting them cool to room temperature. The temperature difference between the deposition temperature and room temperature is ΔT.

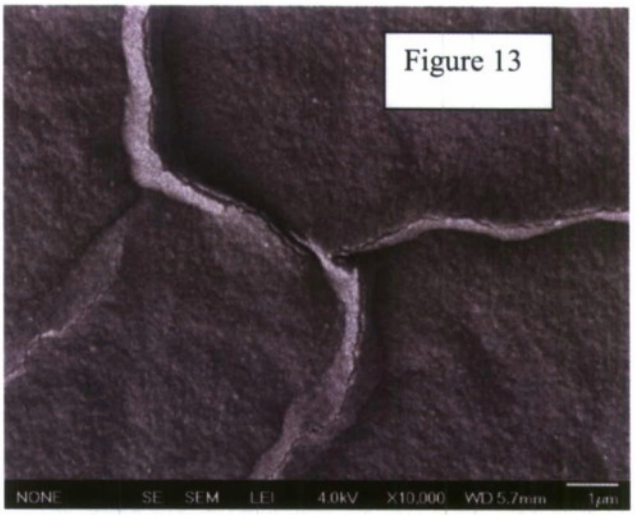
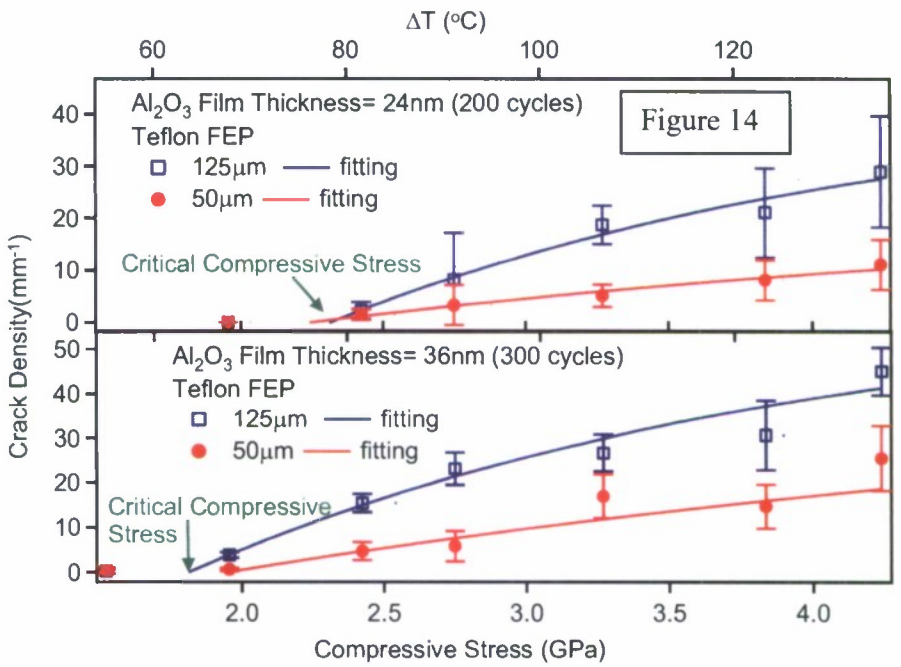
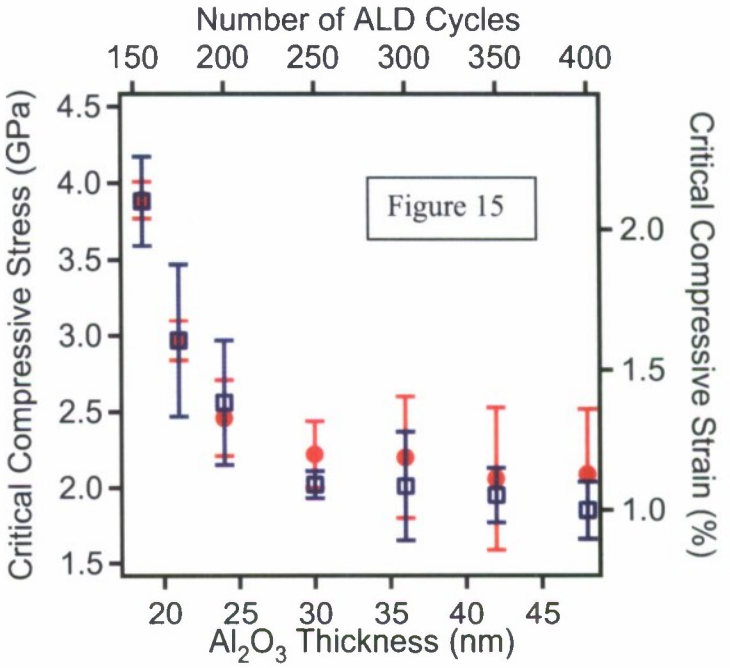


Figure 14 shows the crack density versus compressive stress and the ΔT values that yield these compressive stresses for Al_2O_3 ALD films with thicknesses of 24 nm and 36 nm on Teflon FEP with substrate thicknesses of 50 and 125 μm. The crack threshold is observed at ~2.0 GPa for the 36 nm film and at ~2.5 GPa for the 24 nm film. *Thicker* Al_2O_3 ALD films display *smaller* critical compressive stresses for cracking. We then determined the critical compressive stress for cracking for a variety of Al_2O_3 ALD film thicknesses.



The critical compressive stress for cracking versus Al_2O_3 ALD film thickness is shown in Figure 15. Al_2O_3 ALD film thicknesses were examined from 19-48 nm. The SEM images showed that the films buckled and then cracked with increasing compressive stress. The critical stress for cracking was constant at ~2 GPa for the thicker films with thicknesses >30 nm. The critical stress for cracking increased dramatically to >4 GPa for film thicknesses < 20 nm. These results indicate that thinner Al_2O_3 ALD films are more flexible and able to withstand higher compressive stresses without cracking. Enhanced multilayer gas diffusion barriers should employ thin Al_2O_3 ALD layers for optimum flexibility.



E. Mechanical Measurements on MLD Films and Organic-Inorganic Nanolaminates

In collaboration with colleagues in the Dept. of Mechanical Engineering at the University of Colorado, we also explored the mechanical properties of our MLD films using a nanoindenter. These studies have revealed that the modulus of Al_2O_3 ALD films is 165 GPa. In contrast, the AB alucone MLD film has a lower modulus of 37 GPa. The ABC alucone MLD film has an even lower modulus of 13 GPa. The alucone MLD films will allow us to build various nanolaminate films with tunable and enhanced mechanical properties.

An interesting set of tensile strain measurements was also recently performed on the AB alucone MLD film with a thickness of ~100 nm on PEN. These measurements revealed that the AB alucone has a low critical strain for cracking of 0.7%. The observation of a low critical strain for cracking was not expected because the AB alucone has a low modulus. We expected the AB alucone film to be very flexible and to withstand much higher strains. These results have suggested that the AB alucone MLD films may be easily cracked or "torn" because they have

little cross-linking between the polymer chains. This low critical strain for cracks or "tears" may require us to introduce new ways to increase the cross-linking in alucone MLD films.

We have also used a new focused ion beam (FIB) at the University of Colorado to make cross-sections of the Al_2O_3/alucone MLD/ Al_2O_3 trilayers on PEN. The FIB first cuts the trilayer on the PEN substrate. Subsequently, high resolution SEM can image the trilayer. The resulting SEM image is shown in Figure 16. This image clearly reveals the individual Al_2O_3 ALD and AB alucone MLD layers in the trilayer. The trilayer is very conformal to the underlying PEN substrate and there are well-defined individual layers in the trilayer.

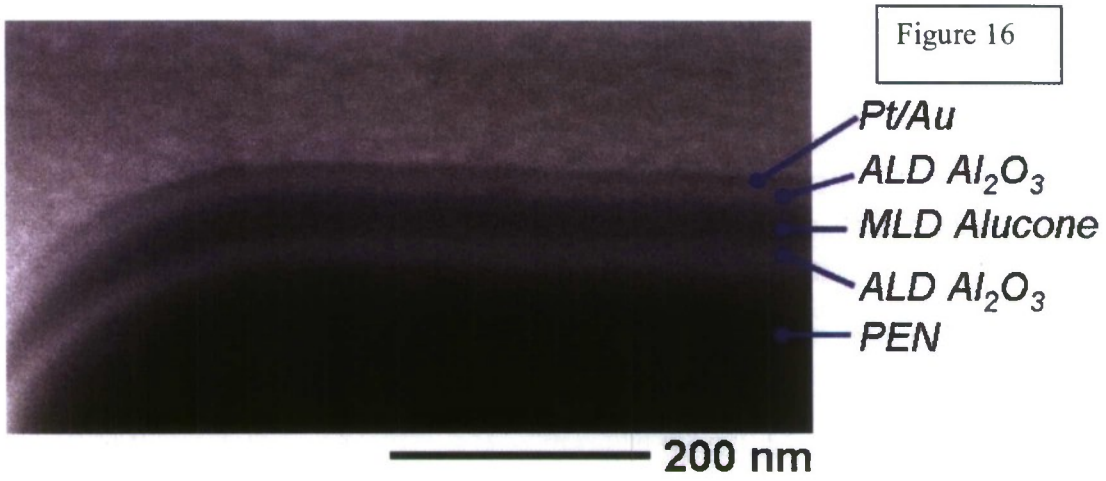


Figure 16

F. New Glovebox Connected to ALD Reactor and PVD Chamber

About six months ago, we completed a new glovebox connected to an ALD reactor and PVD chamber. This new apparatus is now allowing us to deposit Ca films in the PVD chamber and then transfer them through the glovebox to an ALD reactor. This apparatus will be very valuable for fabricating test structures to evaluate ALD films as gas diffusion barriers. In addition, the glove box will allow us to prepare films important for organic electronics and then coat them using ALD without exposure to O_2 or H_2O. Figure 17 shows a diagram of this new experimental apparatus. The ALD reactor has been built on the table of the glovebox. The side panel connecting the glove box to the PVD chamber was modified in the machine shop to allow for sample transfer between the PVD chamber and the glovebox.

Our recent measurements have used the PVD chamber to deposit Ca films on substrates to measure oxidation of the Ca film resulting from H_2O permeability through the ALD gas diffusion barriers. Our results are obtained using a new ALD reactor that is connected to a glove

box that is interfaced to a PVD chamber. This apparatus allows Ca test films to be prepared, transferred into the glove box and then positioned in the ALD reactor all under oxygen-free conditions. The glove box also helps to reduce particle contamination that may be the dominant factor in determining the WVTR.

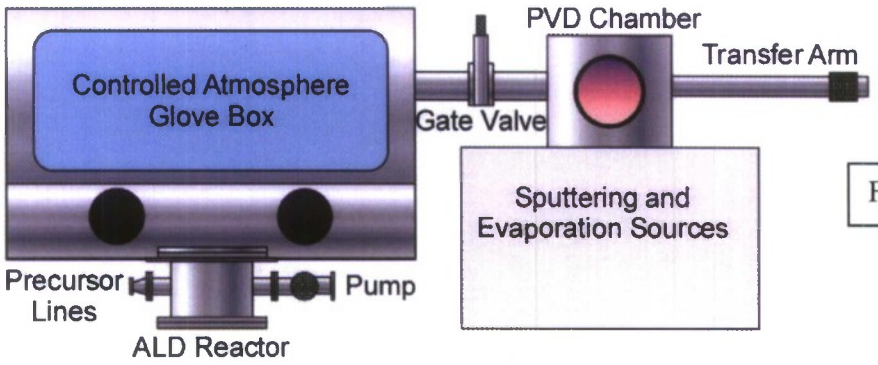


Figure 17

We are employing the Ca test with electrical resistance probing. The electrical resistance probing method is based on previous work by Paetzold and coworkers (*Rev. Sci. Instrum.* 74, 5147 (2003)). The change of the electrical resistance of the Ca film versus time can be related to the WVTR. Using this apparatus, we have measured even lower WVTR values of ~2 x10^{-5} g/m^2/day at 70°C/28% RH with an Al_2O_3 ALD film thickness of 25 nm. This is the lowest WVTR value measured at elevated temperature for a single layer barrier film. The Al_2O_3 ALD barriers are also deposited directly on the Ca films. This configuration allows the Ca test film to visualize the defects in the Al_2O_3 ALD barrier. As the calcium oxidizes, the transition from shiny metal to clear calcium oxide can monitor the number and distribution of defects in the Al_2O_3 ALD film. The experiments demonstrate that the calcium oxidation is dominated by a few pinhole defects. The WVTR value of ~2 x 10^{-5} g/m^2/day is consistent with

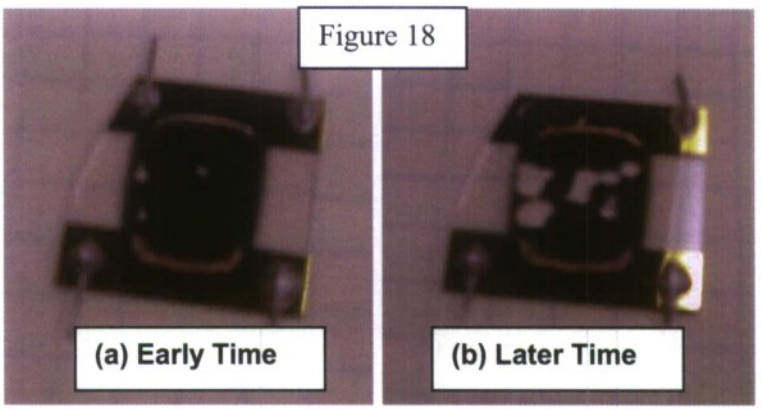


Figure 18

several defects per cm^2 in the Al_2O_3 ALD film. The resistance increases as these pinholes lead to the oxidation of circular regions of the Ca film that grow with time as shown in Figure 18.

E. Protecting Polymers in the Space Environment

Closely related to our gas diffusion barrier work on polymers, we also demonstrated that Al_2O_3 ALD can also be used to protect polymers from erosion by oxygen atoms. In collaborative work with Prof. Tim Minton at Montana State University, we showed that Al_2O_3 ALD films can protect polyimide substrates from corrosion by hyperthermal atomic oxygen beams. The quartz crystal microbalance (QCM) results for the mass change of the polimide polymers spin-coated onto the QCM sensor are shown in Figure 19. Al_2O_3 ALD film thicknesses of only ~3.5 nm were sufficient to protect a polyimide polymer from oxygen atom erosion. These ultrathin Al_2O_3 ALD films may be useful to protect polymers on spacecraft in low Earth orbit. This work led to a Phase I STTR grant from the Air Force. We started the Phase II STTR grant in December 2008.

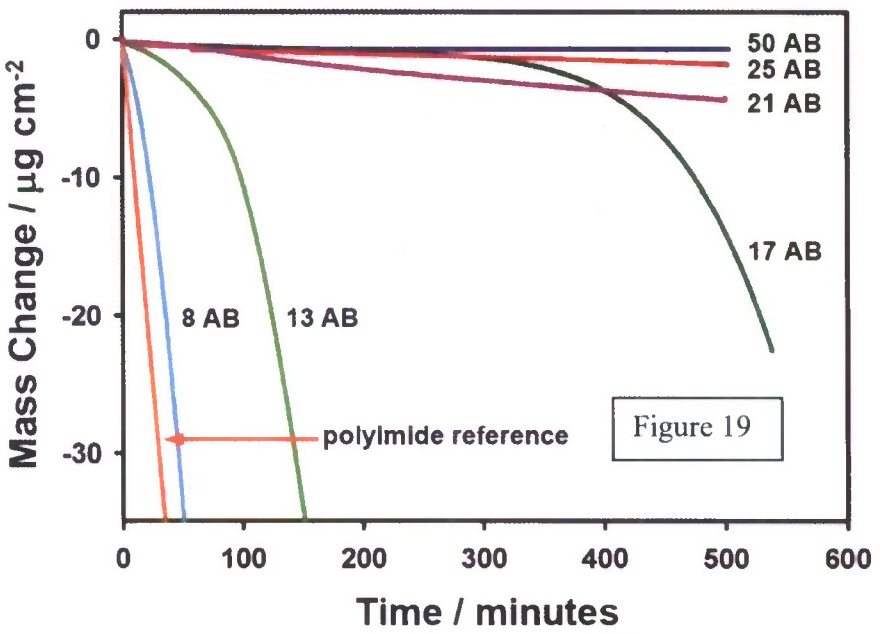


Figure 19

E. Other Collaborations

We have also collaborated with a number of outside groups on ALD applications over the three years of this grant. We have continued to work on applications of ALD for enhanced properties of microelectromechanical systems (MEMS) and ALD for biocompatibile coatings. We are also working to coat nanotubes and nanorods with ALD films through our work in a new DARPA Center centered at the University of Colorado. This new DARPA Center is focused on

Nanoscale Science and Technology for Integrated Micro/Nano-Electromechanical Transducers. These collaborations have been very fruitful and have led to interesting results and publications.

IV. Personnel Supported

Faculty

1. Prof. Steven M. George (One Month Summer Salary)

Postdoctoral Research Associates

1. Dr. Shih-Hui Jen (2007-2008)
2. Dr. Arrelaine Dameron (2006)

Graduate Students

1. Dragos Seghete (Currently Fourth Year Graduate Student)
2. Jaeob Bertrand (Currently Third Year Graduate Student)

Undergraduate Students

1. Jennifer O'Patchen (Summer 2008)

V. Publications

Many manuscripts describing our AFOSR-supported research and collaborations involving our AFOSR-supported research have been published during the last three years. This list includes publications from our parent AFOSR grant (***), publications resulting from AFOSR support through STTR funding (**) and publications using equipment (AFM, XRR and XPS instruments) obtained from AFOSR support through DURIP grants (*).

1. F.H. Fabreguette, R.W. Wind and S.M. George, "Ultra-high X-Ray Reflectivity from W/Al_2O_3 Multilayers Fabricated Using Atomic Layer Deposition", *Appl. Phys. Lett.* **88**, Art. No. 013116 (2006).***

2. M.D. Groner, S.M. George, R.S. McLean and P.F. Carcia, "Gas Diffusion Barriers on Polymers Using Al_2O_3 Atomic Layer Deposition", *Appl. Phys. Lett.* **88**, Art. No. 051907 (2006).*

3. R.K. Grubbs and S.M. George, "Attenuation of Hydrogen Radicals Traveling under Flowing Gas Conditions Through Tubes of Different Materials ", *J. Vac. Sci. Technol. A* **24**, 486-496 (2006).*

4. Z.A. Sechrist, B.T. Schwartz, J.H. Lee, J.A. McCormick, R. Piestun, W. Park, and S.M. George, "Modification of Opal Photonic Crystals Using Al_2O_3 Atomic Layer Deposition", *Chem. Mater.* **18**, 3562-3570 (2006).*

5. P.F. Carcia, R.S. McLean, M.H. Reilly, M.D. Groner and S.M. George, "Ca-Tests of Al_2O_3 Gas Diffusion Barriers Grown by Atomic Layer Deposition on Polymers", *Appl. Phys. Lett.* **89**, 031915 (2006).*

6. M.K. Tripp, C. Stampfer, D.C. Miller, T. Helbling, C.F. Herrmann, C. Hierold, K. Gall, S.M. George and V.M. Bright, "The Mechanical Properties of Atomic Layer Deposited Alumina for Use in Micro- and Nano-Electromechanical Systems", *Sensors and Actuators A* **130-131**, 419-429 (2006).*

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9. D.C. Miller, C.F. Herrmann, H.J. Maier, S.M. George, C.R. Stoldt and K. Gall, "Thermo-Mechanical Evolution of Multilayer Thin Films, Part I: Mechanical Behavior of Au/Cr/Si Microcantilevers", *Thin Solid Films* **515**, 3208-3223 (2007).*

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11. Y. Du, X. Du and S. M. George, "Mechanism of Pyridine-Catalyzed SiO_2 Atomic Layer Deposition Studied by Fourier Transform Infrared Spectroscopy", *J. Phys. Chem. C* **111**, 219-226 (2007).*

12. J.A. McCormick, B.L. Cloutier, A.W. Weimer and S.M. George, "Rotary Reactor for Atomic Layer Deposition on Large Quantities of Nanoparticles", *J. Vac. Sci. Technol. A* **25**, 67-74 (2007).**

13. X.H. Liang, L.F. Hakim, G.D. Zhan, J.A. McCormick, S.M. George, A.W. Weimer, J.A. Spencer II, K.J. Buechler, J. Blackson, C.J. Wood and J.R. Dorgan, "Polymer/Ceramic Nanocomposites Produced by Extruding ALD Nanocoated Polymer Particles," *J. Am Ceram. Soc.* **90**, 57-63 (2007).*

14. J.A. McCormick, K.P. Rice, D.F. Paul, A.W. Weimer and S.M. George, "Al_2O_3 Atomic Layer Deposition on ZrO_2 Nanoparticles in a Rotary Reactor" *Chem. Vapor Depos.* **13**, 491-498 (2007).**

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18. X.H. Liang, S.M. George, A.W. Weimer, N.H. Li, J. Blackson, J. Harris and P. Li, "Synthesis of a Novel Porous Polymer/Ceramic Composite Material by Low-Temperature Atomic Layer Deposition", *Chem. Mater.* **19**, 5388-5394 (2007).*

19. S.M. George, A.A. Dameron, Y. Du, N.M. Adamcyzk and S.D. Davidson, "Molecular Layer Deposition of Organic and Hybrid Organic-Inorganic Films", *Electrochemistry Society (ECS) Transactions* **11**(7), 81-90 (2007) in *Atomic Layer Deposition Applications 3*, edited by A. Londergan, J.W. Elam, O. van der Straten, S. De Gendt, S.F. Bent and S.B. Kang (The Electrochemical Society, Pennington, NJ, 2007).**

20. P.F. Carcia, R.S. McLean, M.D. Groner, A.A. Dameron and S.M. George, "Application of Atomic Layer Deposition for Gas Permeation Barrier Thin Films", *Electrochemistry Society (ECS) Transactions* **11**(7), 15-21 (2007) in *Atomic Layer Deposition Applications 3*, edited by A. Londergan, J.W. Elam, O. van der Straten, S. De Gendt, S.F. Bent and S.B. Kang (The Electrochemical Society, Pennington, NJ, 2007).***

21. A.S. Cavanagh, C.A. Wilson, A.W. Weimer and S.M. George, "Atomic Layer Deposition on Quantities of Multiwalled Carbon Nanotubes", in *Synthesis and Surface Engineering*

of Three-Dimensional Nanostructures, edited by Ruth Hourbertz (Mater. Res. Soc. Symp. Proc. **Volume 1054E**, Warrendale, PA, 2008), Paper #1054-FF03-10.*

22. R. Cooper, H.P. Upadhyaya, T.K. Minton, M.R. Berman, X. Du and S.M. George, "Protection of Polymer from Atomic-Oxygen Erosion Using Al_2O_3 Atomic Layer Deposition Coatings", *Thin Solid Films* **516**, 4036-4039 (2008).**

23. D.S. Finch, T. Oreskovic, K. Ramadurai, C.F. Herrmann, S.M. George and R.L. Mahajan, "Biocompatibility of Atomic Layer-Deposited Alumina Thin Films", *J. Biomed. Mater. Res. A* **87A**, 100-106 (2008).*

24. X. Liang, G.D. Zhan, D.M. King, J.A. McCormick, J. Zhang, S.M. George and A.W. Weimer, "Alumina Atomic Layer Deposition Nanocoatings on Primary Diamond Particles in a Fluidized Bed Reactor", *Diam. Relat. Mater.* **17**, 185-189 (2008).*

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26. C.A. Wilson, J.A. McCormick, A.S. Cavanagh, D.N. Goldstein, A.W. Weimer and S.M. George, "Tungsten Atomic Layer Deposition on Polymers", *Thin Solid Films* **516**, 6175-6185 (2008).**

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36. S.M. George and B. Yoon, "Molecular Layer Deposition of Organic and Hybrid Organic-Inorganic Polymers", In *Material Matters*, Vol. 3, No. 2, "Nanoscale Surface Modification" (Aldrich Chemical Co., Inc., Milwaukee, WI, 2008) pp. 34-37.***

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VI. Interactions/ Transitions

Over the last three years (January 2006-November 2008), the PI has been invited to discuss our AFOSR-supported research or research supported by equipment obtained through AFOSR at many invited talks:

1. "Thin Film Growth Using Atomic Layer Deposition Techniques", Department of Chemistry, Michigan State University, East Lansing, Michigan, March 9, 2006.

2. "Enhanced Thermite Materials by Atomic Layer Deposition of Metal Oxides on Aluminum Nanoparticles", *Second Eglin Symposium on NanoEnergetics (ESNE2)*, Research, Engineering and Education Facility (REEF) of the University of Florida, Shalimar, Florida, March 22, 2006.

3. "Fabrication and Properties of Al_2O_3/W Nanolaminates Prepared Using Atomic Layer Deposition Techniques", Physical Chemistry and Spectroscopy, Los Alamos National Laboratory, Los Alamos, New Mexico, April 13, 2006.

4. "Atomic Layer Deposition on Particles", *Symposium on "Fundamental Gas-Phase and Surface Chemistry of Vapor-Phase Materials Processing III"*, 209th Meeting of the Electrochemistry Society, Denver, Colorado, May 10, 2006.

5. "Atomic Layer Deposition of Ceramic Films on Polymers", *Session on Surface Engineering with Ceramics, Surface Processing Science*, International Conferences on Modern Materials and Technologies (CIMTEC 2006), Acireale, Sicily, Italy, June 6, 2006.

6. "Atomic Layer Deposition of Polymers", AVS Topical Conference on Atomic Layer Deposition (ALD2006), Hotel-Seoul Kyoyuk MunHwa HoeKwan, Seoul, Korea, July 24, 2006.

7. "Molecular Layer Deposition of Organic/Inorganic Hybrid Films", Dept. of Chemistry, Hanyang University, Scoul, Korea, July 27, 2006.

8. "Tantalum Nitride Atomic Layer Deposition Using TBTDET and Hydrogen Radicals, Hydrazine or NH_3", Research and Development Division, Hynix Semiconductor, Inc., Ami-ri Bubal-eub Icheon-si Kyoungki-do, Korea, July 28, 2006.

9. "Atomic Layer Deposition of Polymers", Analytical Chemistry Departmental Seminar, Dept. of Chemistry, University of Colorado, September 18, 2006.

10. "Atomic Layer Deposition of Polymers", Qualcomm MEMS Technologies, San Jose, California, November 15, 2006.

11. "Atomic Layer Deposition of Polymers", Aixtron-Genus, Sunnyvale, California, November 15, 2006.

12. "Atomic Layer Deposition of Polymers", Applied MicroStructures, Inc., San Jose, California, November 16, 2006

13. "Atomic Layer Deposition of Polymers", Lam Research Corporation, Fremont, California, November 16, 2006.

14. "Atomic Layer Deposition on Polymers and Polymer Molecular Layer Deposition", Advanced Materials and Processes Laboratory, Hewlett-Packard Company, Corvalis, Oregon, November 3, 2006.

15. "Atomic Layer Deposition on Nanoparticles", Nanoparticle Science & Engineering Seminar, University of Minnesota, Minneapolis, Minnesota, December 15, 2006.

16. "Atomic Layer Deposition on Polymers & Molecular Layer Deposition of Polymers", ZettaCore Inc., Englewood, Colorado, March 15, 2007.

17. "Atomic Layer Deposition for Thin Film Growth", ASM America Inc., Phoenix, Arizona, March 29, 2007

18. "Atomic Layer Deposition of Copper Barrier and Seed Films", Novellus Fourth International Copper Interconnect Technology Symposium, Tsinghua University, Beijing, China, May 28, 2007.

19. "Atomic Layer Deposition of Copper Barrier and Seed Films", Novellus Fourth International Copper Interconnect Technology Symposium, Fudan University, Shanghai, China, May 30, 2007.

20. "Molecular Layer Deposition of Organic and Hybrid Organic-Inorganic Thin Films", Gordon Research Conference on the *Chemistry of Electronic Materials*, Mount Holyoke College, July 25, 2007.

21. "Molecular Layer Deposition of Alucone and other Organic-Inorganic Polymers", Division of Inorganic Chemistry, Symposium on *Thin Films: Chemical Vapor Deposition and Atomic Layer Deposition*, American Chemical Society Meeting, Boston, Massachusetts, August 20, 2007.

22. "SiO Atomic Layer Deposition Using Catalyzed Surface Reactions and Silanol Polymerization", Sigma-Aldrich Fine Chemicals, Sheyboygan, Wisconsin, September 6, 2007.

23. "Gas Diffusion Barriers on Polymers Using Atomic Layer Deposition Techniques", Analytical Chemistry Division Seminar, Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, September 17, 2007.

24. "The Potato Chip Bag Problem: Gas Diffusion Barriers on Polymers", Physical Chemistry Division Seminar, Department of Chemistry and Biochemistry, University of

Colorado, Boulder, Colorado, September 21, 2007.

25. "Atomic Layer Deposition: Fundamentals and Applications" (Invited Short Course), Sociedad Mexicana de Ciencia y Tecnologia de Superficies y Materiales (SMCTSM), XXVII Congreso Nacional, Oaxaca, Oaxaca, Mexico, September 26, 2007.

26. "Atomic Layer Deposition of Nanolaminates: Fabrication and Properties" (Plenary Lecture), Sociedad Mexicana de Ciencia y Tecnologia de Superficies y Materiales (SMCTSM), XXVII Congreso Nacional, Oaxaca, Oaxaca, Mexico, September 27, 2007.

27. "Molecular Layer Deposition of Organic and Hybrid Organic-Inorganic Films", 212th Meeting of the Electrochemical Society, Session on *Atomic Layer Deposition Applications 3*, October 9, 2007

28. "The Potato Chip Bag Problem: Gas Diffusion Barriers on Polymers", Department of Chemical and Petroleum Engineering, Colorado School of Mines, Golden, Colorado, November 2, 2007.

29. "Atomic Layer Deposition", Invited Tutorial at Fall Meeting of the Materials Research Society, in Symposium FF on *Synthesis and Surface Engineering of Three-Dimensional Nanostructures*, Boston, Massachusetts, November 25, 2007

30. "Atomic Layer Deposition on Quantities of Multiwalled Carbon Nanotubes", Fall Meeting of the Materials Research Society, in Symposium FF on *Synthesis and Surface Engineering of Three-Dimensional Nanostructures*, Boston, Massachusetts, November 27, 2007.

31. "Molecular Layer Deposition of Organic and Hybrid Organic-Inorganic Polymers", Micronova /Helsinki University of Technology, Espoo, Finland, April 28, 2008.

32. "Rapid SiO_2 ALD Using Silanol Precursors", Micronova /Helsinki University of Technology, Espoo, Finland, April 28, 2008.

33. "Atomic Layer Deposition on Polymers for Diffusion Barriers", Micronova /Helsinki University of Technology, Espoo, Finland, April 29, 2008.

34. "Nucleation of Pd ALD on Al_2O_3 Surfaces", Micronova /Helsinki University of Technology, Espoo, Finland, April 29, 2008.

35. "Rapid SiO_2 ALD Using Silanol Precursors", UP Chemical Co., Ltd, 576-2 Chilgwe-Dong Pyeongtaek, Korea, May 29, 2008.

36. "Molecular Layer Deposition of Organic and Hybrid Organic-Inorganic Polymers", 4th Korean ALD Workshop, Hangyang University, Seoul, Korea, May 30, 2008.

37. "Molecular Layer Deposition of Organic and Hybrid Organic-Inorganic Polymers", Sundew Technologies, LLC, Broomfield, CO, June 18, 2008.

38. "Surface Chemistry for Atomic Layer Deposition and Molecular Layer Deposition:

Current Understanding and Future Prospects", 8th International Conference on Atomic Layer Deposition, (ALD2008), Bruges, Belgium, June 29, 2008.

39. "Surface Chemistry for Molecular Layer Deposition of Polymers", Germany ALD Workshop 2008 (GerALD 2008), Max Planck Institute of Microstructure Physics, Halle, Germany, September 22, 2008.

40. "Molecular Layer Deposition of Organic and Hybrid Organic-Inorganic Polymers", Analytical Chemistry Seminar, Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, September 29, 2008.

41. "Molecular Layer Deposition of Organic and Hybrid Organic-Inorganic Polymers", Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware, October 8, 2008.

42. "Molecular Layer Deposition of Organic and Hybrid Organic-Inorganic Polymers", DuPont Research and Development, Experimental Station, Wilmington, Delaware, October 9, 2008.

43. "Molecular Layer Deposition of Organic and Hybrid Organic-Inorganic Polymers", Department of Chemistry, Northwestern University, Evanston, Illinois, November 7, 2008.

The PI and other members of the research group have also presented the results of our work as contributed talks or posters at various meetings and conferences. This work includes AFOSR-supported studies, research supported by equipment obtained through AFOSR and various AFOSR-collaborations:

Contributed Talks:

1. "Tantalum Nitride Atomic Layer Deposition Using TBTDET and Hydrogen Radicals, Hydrazine or NH_3", G.B. Rayner, B.B. Burton, S.M. George and A.R. Lavoie, AVS Topical Conference on Atomic Layer Deposition (ALD2006), Hotel-Seoul Kyoyuk MunHwa HoeKwan, Seoul, Korea, July 24, 2006.

2. "In Situ Resistance Study of Tin Oxide ALD and Thickness Effects on CO Gas Sensing", X. Du, Y. Du and S.M. George, AVS Topical Conference on Atomic Layer Deposition (ALD2006), Hotel-Seoul Kyoyuk MunHwa HoeKwan, Seoul, Korea, July 24, 2006.

3. "Mechanism of Al_2O_3 Atomic Layer Deposition Using Trimethylalumunim and Ozone", D.N. Goldstein and S.M. George, Atomic Layer Deposition of Polymers", AVS Topical Conference on Atomic Layer Deposition (ALD2006), Hotel-Seoul Kyoyuk MunHwa HoeKwan, Seoul, Korea, July 25, 2006.

4. "MnO and MgO Atomic Layer Deposition Using Bis(Ethylcyclopentadienyl) Precursors and H_2O", B.B. Burton, F.H. Fabreguette, D.N. Goldstein and S.M. George, AVS Topical

Conferencc on Atomic Layer Deposition (ALD2006), Hotel-Scoul Kyoyuk MunHwa HoeKwan, Seoul, Korea, July 25, 2006.

5. "Mechanism of Al_2O_3 Atomic Layer Deposition Using Trimethylalumunim and Ozone", D.N. Goldstein and S.M. George, *Thin Film Division Session on ALD and Applications*, 53rd International Symposium of the American Vacuum Society, Moscone West, San Francisco, November 13, 2006.

6. "MnO and MgO Atomic Layer Deposition Using Bis(Ethylcyclopentadienyl) Precursors and H_2O", B.B. Burton, F.H. Fabreguette, D.N. Goldstein and S.M. George, *Thin Film Division Session on ALD and Applications*, 53rd International Symposium of the American Vacuum Society, Moscone West, San Francisco, November 13, 2006.

7. "Molecular Layer Controlled Deposition of Polymer Thin Films", A.A. Dameron, Y.Du, N.M. Adamczyk and S.M. George, *Thin Film Division Session on ALD and Applications*, 53rd International Symposium of the American Vacuum Society, Moscone West, San Francisco, November 13, 2006.

8. "Gas Diffusion Barriers on Polymers Using Al_2O_3 Atomic Layer Dcposition", M.D. Groner, A.A. Dameron, R.S. McLean, P.F. Carcia and S.M. George, *Thin Film Division Session on ALD and Applications*, 53rd International Symposium of the American Vacuum Society, Moscone West, San Francisco, November 13, 2006.

9. "Rapid ALD of SiO_2 Using Tris(tert-pentoxy)Silanol", B.B. Burton and S.M. George, ASM America, Inc., March 29, 2007.

10. "Ruthenium Atomic Layer Deposition with RuO_4 (ToRuS)", D.N. Goldstein and S.M. George, ASM America, Inc., March 29, 2007.

11. "Molecular Layer Deposition of Alucone Polymer Films Using Trimethylaluminum and Ethylene Glycol", A.A. Dameron, S.D. Davidson, B.B. Burton, J.A. McCormick, A.S. Cavanagh and S.M George, AVS 7th International Conference on Atomic Layer Deposition (ALD2007), Kona Kai Resort, San Diego, California, June 26, 2007.

12. "Nanolaminate Gas Diffusion Barriers on Polymers with Exceptionally Low H_2O Permeabilities", A.A. Dameron, S.M. George, P.F. Carcia and R.S. McLean, AVS 7th International Conference on Atomic Layer Deposition (ALD2007), Kona Kai Resort, San Diego, California, June 26, 2007.

13. "Quadrupole Mass Spectrometry Analysis of Al_2O_3 ALD on Nanoparticles Using H_2O and O_3 as Oxidants", J.A. McCormick, A.W. Weimer and S.M. George, AVS 7th International Conference on Atomic Layer Deposition (ALD2007), Kona Kai Resort, San Diego, California, June 27, 2007.

14. "Laterally Graded Layers of Al_2O_3 Atomic Layer Deposition", D. Seghete and S.M. George, AVS 7th International Conference on Atomic Layer Deposition (ALD2007), Kona Kai Resort, San Diego, California, June 27, 2007.

15. "Atomic Layer Deposition of Al_2O_3 and W/Al_2O_3 on Quantities of Multiwalled Carbon

Nanotubes", A.S. Cavanagh, C.A. Wilson and S.M. George, AVS 7th International Conference on Atomic Layer Deposition (ALD2007), Kona Kai Resort, San Diego, California, June 27, 2007.

16. "Application of Atomic Layer Deposition for Gas Permeation Barrier Thin Films", P.F. Carcia, R.S. McLean, M.D. Groner, A.A. Dameron and S.M. George, 212th Meeting of the Electrochemical Society, Session on *Atomic Layer Deposition Applications 3*, October 8, 2007

17. "Atomic Layer Deposition of Al_2O_3 and W/Al_2O_3 on Quantities of Multiwalled Carbon Nanotubes", A.S. Cavanagh, C.A. Wilson, and S.M. George, Thin Film Division Session on *Atomic Layer Deposition*, International AVS Symposium, Seattle, Washington, October 15, 2007.

18. "Nanolaminate Gas Diffusion Barriers on Polymers with Exceptionally Low H_2O Permeabilities", A.A. Dameron, S.M. George, P.F. Carcia and R.S. McLean, Thin Film Division Session on *Atomic Layer Deposition*, International AVS Symposium, Seattle, Washington, October 15, 2007.

19. "Fabrication of Hybrid Inorganic/Organic Multilayers Using Atomic and Molecular Layer Deposition", D. Seghete, A.A. Dameron, S.D. Davidson, J.A. Bertrand, B.B. Burton, J.A. McCormick, A.S. Cavanagh and S.M. George, Thin Film Division Session on *Atomic Layer Deposition*, International AVS Symposium, Seattle, Washington, October 15, 2007.

20. "Molecular Layer Deposition of Alucone Polymer Films Using Trimethylaluminum and Various Glycols", A.A. Dameron, S.D. Davidson, B.B. Burton, J.A. McCormick, A.S. Cavanagh and S.M. George, Thin Film Division Session on *Atomic Layer Deposition*, International AVS Symposium, Seattle, Washington, October 15, 2007.

21. "Palladium Nucleation on Oxide Substrates during Palladium Atomic Layer Deposition", D. N. Goldstein and S.M. George, Thin Film Division Session on *Atomic Layer Deposition*, International AVS Symposium, Seattle, Washington, October 16, 2007.

22. "Growth Kinetics and Mechanism of Rapid SiO_2 Atomic Layer Deposition Using Tris(tert-Pentoxy)Silanol", Beau B. Burton and Steven M. George, 8th International Conference on Atomic Layer Deposition, (ALD2008), Bruges, Belgium, June 30, 2008.

23. "Molecular Layer Deposition of Hybrid Organic-Inorganic Polymers Based on Metal Alkyl and Diol Reactants", Byunghoon Yoon, Jennifer L. O'Patchen, Stephen D. Davidson, Dragos Seghete, Andrew S. Cavanagh and Steven M. George, 8th International Conference on Atomic Layer Deposition, (ALD2008), Bruges, Belgium, July 2, 2008.

24. "New Approaches to Molecular Layer Deposition Using Ring-Opening and Heterobifunctional Reactants", Dragos Seghete, Byunghoon Yoon, Andrew S. Cavanagh and Steven M. George, 8th International Conference on Atomic Layer Deposition, (ALD2008), Bruges, Belgium, July 2, 2008.

25. "Growth Kinetics and Mechanism of Rapid SiO_2 Atomic Layer Deposition Using

Tris(tert-Pentoxy)Silanol", Beau B. Burton and Steven M. Georgc, AVS 55th International Symposium, Boston, Massachusetts, Oetober 20, 2008.

26. "Moleeular Layer Deposition of Hybrid Organic-Inorganic Polymers Based on Metal Alkyl and Diol Reaetants", Byunghoon Yoon, Jennifer L. O'Patehen, Stephen D. Davidson, Dragos Seghete, Andrew S. Cavanagh and Steven M. Gcorge, AVS 55th International Symposium, Boston, Massachusctts, October 20, 2008.

27. "New Approaches to Molccular Layer Deposition Using Ring-Opening and Heterobifunctional Reaetants", Dragos Seghete, Byunghoon Yoon, Andrew S. Cavanagh and Steven M. George, AVS 55th Intcrnational Symposium, Boston, Massaehusetts, Oetober 20, 2008.

28. "Atomic Layer Deposition (ALD) and Molecular Layer Deposition (MLD) for Barrier Coatings on Polymers" Dragos Seghete, Shih-Hui Jen, Jaeob A. Bertrand, Steven M. George, IMAPS/ACerS 2009 International Conference and Exhibition on *Ceramic Interconnect and Ceramic Microsystems Technologies* (CICMT), Denver, Colorado, April 21, 2009.

29. "Defcet Inspection of ALD/MLD-Based Barrier Coatings", Yadong Zhang, Yu-Zhong Zhang, David C. Miller, Jaeob A. Bertrand, Shih-Hui Jcn, Ronggui Yang, Martin L. Dunn, Steven M. George and Y. C. Lee, IMAPS/ACerS 2009 International Conferenee and Exhibition on *Ceramic Interconnect and Ceramic Microsystems Technologies* (CICMT), Denver, Colorado, April 21, 2009.

30. "Mechanical Robustness of ALD/MLD-Based Barreir Coatings", David C. Miller, Ross R. Foster, Yadong Zhang, Shih-Hui Jen, Jaeob A. Bertrand, Zhixing Lu, Dragos Seghete, Jennifer L. O'Patchen, Ronggui Yang, Yung-Cheng Lee, Steven M. George and Martin L. Dunn, IMAPS/ACerS 2009 International Conferenee and Exhibition on *Ceramic Interconnect and Ceramic Microsystems Technologies* (CICMT), Denver, Colorado, April 21, 2009.

31. "Flexible Thermal Ground Plane Enabled by ALD/MLD-Based Barrier Coatings", Ching-Yi Lin, Ronggui Yang, Y. C. Lee, Aziz Abdulagatov, Steven M. George, IMAPS/ACerS 2009 International Conferenee and Exhibition on *Ceramic Interconnect and Ceramic Microsystems Technologies* (CICMT), Denver, Colorado, April 21, 2009.

Posters:

1. "Atomie Layer Deposition of Thin Films for Nanostrueture Fabrication and Engincering", S.M. George, CU/NREL Renewable Energy Symposium, University of Colorado, Boulder, Colorado, Oetober 3, 2006.

2. "Meehanism of Al_2O_3 Atomie Layer Deposition Using TMA and Ozone", D.N. Goldstein and S.M. George , Rocky Mountain Chapter American Vacuum Society Meeting, Colorado Sehool of Mines, Golden, Colorado, September 21, 2006.

3. "In Situ Resistance Study of Tin Oxide Atomic Layer Deposition and Thiekness Effects on CO Gas Sensing", Xiaohua Du, Yijun Du and S.M. George , Rocky Mountain

Chapter American Vacuum Society Meeting, Colorado School of Mines, Golden, Colorado, September 21, 2006.

4. "Laterally Graded Layers by Atomic Layer Deposition", Dragos Seghete and S.M. George, Rocky Mountain Chapter American Vacuum Society Meeting, Colorado School of Mines, Golden, Colorado, September 21, 2006.

5. "Understanding the Long Nucleation Period for Pd ALD on Al_2O_3 Substrates", D.N. Goldstein and S.M. George, Rocky Mountain AVS Meeting, Golden, CO, September 27, 2007.

6. "Atomic Layer Deposition of Y_2O_3 Using Tris(butylcyclopentadienyl)yttrium and Water, Aziz I. Abdulagotov and Steven M. George, Rocky Mountain AVS Meeting, Golden, CO, September 27, 2007.

7. "Synthesis and Characterization of Hybrid Organic-Inorganic Thin Films via Atomic Layer Deposition for MEMS/NEMS," D. Seghete, Y.J. Chang, B.D. Davidson, V.M. Bright, and S.M. George, Hilton Head Workshop 2008: A Solid-State Sensors, Actuators, and Microsystems Workshop, Hilton Head, South Carolina, June 2-5, 2008.

8. "Sacrificial Layers for Air Gaps in NEMS using Alucone Molecular Layer Deposition", D. Seghete, B. D. Davidson, R. A. Hall, Y. J. Chang, V. M. Bright and S. M. George, Rocky Mountain AVS Meeting, Golden, Colorado, September 11, 2008.

9. "Trimethylgallium, a New Precursor for Ga_2O_3 ALD", D.N. Goldstein and S.M. George, Rocky Mountain AVS Meeting, Golden, Colorado, September 11, 2008.

Collaborations

The results from our AFOSR-sponsored research on ALD and nanolaminates grown using ALD are technologically relevant. Atomic layer deposition (ALD) techniques have many useful industrial applications. In the past, our results have been implemented by the semiconductor industry. The most prominent example is W ALD. We initially developed W ALD to fabricate Al_2O_3/W ceramic/metal nanolaminates for superior thermal barrier coatings. Our W ALD process is now being used for contact hole filling. The self-limiting surface chemistry that we developed for W ALD is used by Applied Materials (Sunnyvale, Calif.) and Novellus (San Jose, Calif.) as a W seed in contact holes for W chemical vapor deposition (CVD). W CVD is used to fill the contact holes in the first level of backend interconnects.

Our ALD-supported by AFOSR has also found many applications for MEMS. We have collaborations with several groups in the Mechanical Engineering Department and the DARPA Center for *Nanoscale Science and Technology for Integrated Micro/Nano-Electromechanical Transducers* at the University of Colorado. This work has been very productive. Our previous work on Al_2O_3 ALD on carbon nanotubes (CNTs) was utilized as a focus of the new DARPA Center (http://www.imintcenter.org/). ALD processing of nanotubes and nanorods is the main fabrication technique to build nanosensors and nanotransducers.

Over the last three years, we also have deposited a variety of ALD films on different devices and substrates for various industries, national laboratories and universities. A list of our collaborations over the last three years is given below.

A. Synkera Technologies, Inc. Synkera Technologies, Inc. is a startup in Longmont, Colorado, that is focused on various nanotechnologies. Over the last three years, we have worked with them on Phase I and Phase II SBIR programs. The Phase I program has focused on GaN and InN ALD for the fabrication of tunable bandgap photovoltaic devices. The Phase II program has worked on Y_2O_3 ALD into the pores of anodic aluminun oxide to fabricate a robust infrared window.

B. ALD NanoSolutions. ALD NanoSolutions is a startup founded by the PI and Prof. Al Weimer in the Dept. of Chemical and Biological Engineering at the University of Colorado. During the last three yeasr, we have worked with ALD NanoSolutions on two Phase I SBIR programs. One Phase I SBIR Program funded from January 1, 2008 - December 31, 2008

through the NSF is "Flexible Inorganic/Polymer Multilayer Gas Diffusion Barrier Films". The second Phase I STTR Program funded from September 15, 2007 - June 14, 2008 through AFOSR was "Atomic Layer Deposition to Protect Polymers in Space". We also began a new Phase II STTR Program in December 2008 that continues our work on using ALD to protect polymers from damage in space.

C. DuPont Research & Development. Over the last three years, we have continued our collaboration with DuPont on gas diffusion barriers on polymers. We received no direct funding from DuPont. However, we collaborated on the testing of the gas diffusion barriers fabricated using ALD methods. DuPont has the instrumentation to perform the Ca test of H_2O permeability. Our work last focused on Al_2O_3/SiN gas diffusion barriers.

D. ASM America, Inc. In April 2007, we initiated a research program with ASM American, Inc. ASM is a manufacturer of equipment for semiconductor processing. During this one year program, we have explored rapid SiO_2 ALD using various silanol molecules and Ru ALD and CVD using RuO_4 as the ruthenium precursor.

E. Dynamic Organic Light, Inc. We started working with Dynamic Organic Light in early 2007. Dynamic Organic Light is a startup company in Longmont, Colorado, that is working to commercialize high brightness organic light emitting diodes (OLEDs). We worked with them to demonstrate the effectiveness of ALD gas diffusion barriers on the OLEDs to prevent failure from H_2O and O_2 permeability. Unfortunately, Dynamic Organic Light went out of business in July 2008.

F. National Renewable Energy Laboratory (NREL). During the last year, we initiated a collaboration with NREL through the CU/NREL Energy Initiative. We received $45,000 as a seed grant for the period July 1, 2007 - June 30, 2009 to work on "Solar Cell Based on Interpenetrating Network of II-VI Semiconductor Nanowires in Oriented TiO_2 Nanotube Array".

G. University of Minnesota - Subcontract from DOE. We have a subcontract from the University of Minnesota to deposit W ALD and Mo ALD on photonic crystals. The title of the program is "Modification of Thermal Emission via Photonic Crystals". The goal is to build a better lightbulb by restricting the emission of infrared light and channeling all thermal emission into the visual spectrum.

VII. New Discoveries, Inventions or Patent Disclosures

The University of Colorado has received and applied for a variety of patents based on the research in Prof. Steven George's research group that has been supported by AFOSR. Previous awarded patents based on AFOSR support include:

1. J.W. Klaus, O.Sneh and S.M. George, "Method of Growing Films on Substrates at Room Temperature Using Catalyzed Binary Reaction Sequence Chemistry", U.S. Patent 6,090,442, July 18, 2000.

2. J.W. Klaus and S.M. George, "Method for Forming SiO_2 by Chemical Vapor Deposition at Room Temperature", U.S. Patent Number 6,818,250, November 16, 2004.

3. J.W. Klaus and S.M. George, "A Solid Material Comprising a Thin Metal Film on its Surface and Methods for Producing the Same", U.S. Patent 6,958,174, October 2005.

4. V.M. Bright, J.W. Elam, F. Fabreguette, S.M. George, N. Hoivik, Y.C. Lee, R. Linderman and M. Tripp, "Atomic Layer Deposition on Micro-Mechanical Devices", U.S. Patent 7,426,067, September 16, 2008.

Patent applications based on AFOSR support currently under review include:

1. S.M. George and C.R. Herrmann, "Al_2O_3 Atomic Layer Deposition to Enhance the Deposition of Hydrophobic or Hydrophyllic Coatings on Microelectromechanical Devices", U.S. Patent Application Number 20050012975.

2. S.J. Henderson and S.M. George, "High Reflectivity and Ultra-High Flux X-ray Optical Element Based on a Graded Multilayer Inside a Monocapillary Tube Fabricated Using Atomic Layer Deposition Techniques", U.S. Patent Application, filed PCT.

3. S.M. George, A.A. Dameron and N.M. Adamczyk, "Molecular Layer Deposition Process for Making Organic or Organic-Inorganic Polymers", University of Colorado Docket Number UTC 014. Full Patent Filed Fall 2007).

4. A.A. Dameron and S.M. George, "Protective Coatings for Organic Electronic Devices Made Using Atomic Layer Deposition and Molecular Layer Deposition Techniques", University of Colorado Docket Number UTC 016, app. No. 60/939,818. (Full Patent Filed Spring 2008).

VIII. Honors/Awards

Over the last three years, Prof. Steven M. George has received awards from the University of Colorado. In 2006, he received the Faculty Research Award from the College of Engineering and Applied Science and the Boulder Faculty Assembly Excellence in Research Scholarly & Creative Work Award. In 2008, he received the 2008 Dean's Award for Outstanding Research in the College of Engineering.

Prof. George is also very active in the American Vacuum Society (AVS). He was elected by the AVS membership to serve as an AVS Trustee (January 2007-December 2009) and on the Executive Board of the Thin Film Division (January 2007-December 2008). He is currently Chair of the AVS Trustees (January 2009-December 2009). Prof. George has also been previously elected a Fellow in the American Vacuum Society (2000) and a Fellow in the American Physical Society (1997).